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MAJOR ION CHEMISTRY OF THE PRE-MELT SNOWPACK, TURKEY LAKES WATERSHED, 1980-1988

by
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ABSTRACT

Composite cores from the pre-melt snowpack were collected at 11 sites in the Turkey Lakes Watershed during the period 1981 to 1988. Annual mean water equivalence ranged from 159 to 377mm. The chemical composition of the snow cover reflected the anthropogenic source of the major ions as shown by levels of H^+ , NO_3 and SO_4 which constituted about 70% of the total ionic content. Both concentrations and ion loadings were influenced by the water equivalence: peak snowpack concentrations paralleled minimum water content whereas maximum loadings coincided with high water equivalence values. The annual trend in the equivalent ratios of SO_4/NO_3, H/SO_4 and H/NO_3 supported the hypothesis that H^+ and NO_3 levels in snowfall have increased with respect to SO_4 since 1980. Snowpack concentrations averaged over the basin were generally less than levels in cumulative wet-only deposition, a discrepancy attributable primarily to inter-site variability in the snow cover.

RÉSUMÉ

On a prélevé des carottes composites de pack nival à douze endroits dans le bassin versant des lacs Turkey, avant la période de fonte, entre 1981 et 1988. La valeur annuelle de l'équivalence moyenne en eau variait de 159 à
377 mm. La composition chimique de la couverture nivale témoignait de l'origine anthropique des ions majeurs; en effet, le H^+, le NO_3 et le SO_4 représentaient plus de 70 % de toutes les espèces ioniques présentes. L'équivalence en eau influait sur les concentrations et les charges en espèces ioniques: les concentrations dans le pack nival devenaient maximales lorsque la teneur en eau était minimale, tandis que les charges maximales coincidaient à des valeurs élevées de l'équivalence en eau. La tendance annuelle des rapports SO_4/NO_3, H/SO_4 et H/NO_3 confirmait l'hypothèse que les concentrations de H^+ et de NO_3 dans les précipitations de neige ont augmentées par rapport aux concentrations de SO_4 depuis 1980. Les concentrations moyennes dans le pack nival pour le bassin versant étaient généralement plus faibles que les concentrations dans les précipitations cumulatives constituées uniquement d'eau; cet écart était attribuable principalement à la variabilité inter-sites de la couverture nivale.

MANAGEMENT PERSPECTIVE

Implications of the snowpack study at the Turkey Lakes Watershed must be taken in context to the objectives of the larger NWRI mass balance program at this site, e.g., to evaluate the geochemical processes regulating basin acidification. These results show that the pre-melt snow cover is an effective medium for monitoring atmospheric deposition. Loadings of H^+, SO_4 and NO_3, which are ultimately delivered to terrestrial and aquatic sectors during periods of snowmelt, are influenced primarily by the water content of the snowpack. Annual records of snowpack chemistry, from 1980 to 1988, indicate a trend of increasing H^+ and NO_3 concentrations relative to SO_4 levels which attests to the evolving role of nitrate in basin acidification, at least during the winter and spring months.

PERSPECTIVE-GESTION

Les tendances que révèle l'étude du pack nival effectuée dans le bassin ersant des lacs Turkey doivent être considérées dans le contexte des objectifs u programme de détermination du bilan massique, qui est de plus grande nvergure, mis en oeuvre dans cette région par l'INRE, par exemple l'évaluation es processus géologiques qui régissent l'acidification du bassin. Ces ésultats montrent que la couverture nivale constitue, avant la période de onte, un bon milieu pour déterminer l'importance des dépôts atmosphériques. es charges de H^+, de SO_4 et de NO_3 qui, en fin de compte, sont déposées ans les environnements terrestres et aquatiques pendant les périodes de fonte ont surtout influencées par la teneur en eau de la couverture nivale. Les onnées historiques sur la chimie du pack nival au cours de la période 1980 - 988 indiquent que les concentrations de H^+ et de NO_3 ont tendance à ugmenter par rapport aux concentrations de SO_4, ce qui témoigne du rôle de lus en plus important que jouent les nitrates dans l'acidification du bassin ydrographique, du moins à l'hiver et au printemps.

INTRODUCTION

The Turkey Lakes Watershed (TLW) is the site of multi-disciplinary studies into the aquatic and terrestrial effects of the long range transport of air pollutants. As a consequence of the significant contribution of snowmelt to the hydrological flux and to the biogeochemical cycling of major ions and nutrients in the basin, long-term research has been established to elucidate the physical and chemical properties of the parent snowpack (English et al., 1987; Semkin and Jeffries, 1988). Furthermore, the pre-melt snowpack is an effective composite of wet and dry atmospheric deposition through the winter months, and can be used to monitor the temporal changes in atmospheric deposition resulting from various emission patterns.

STUDY AREA

The TLW, an area of 10.5 km^2, is located on the Precambrian Shield some 60 km north of Sault Ste. Marie, Ontario. Drainage is southward into Lake Superior. The forest cover is predominantly hardwood consisting of sugar maple and yellow birch. Conifers account for approximately 1% of the total phytomass in upland areas and higher proportions in lowland sites. Annual precipitation from 1981 to 1988 averaged 1248 mm of which about 30% occurred as snow. Details on the physical, chemical and biological characteristics of the watershed are provided by Jeffries et al. (1988).

METHODS

Cores were routinely collected from the TLW snowpack both before and during the spring melt period. By selecting surveys where sub-zero temperatures prevailed, and where the snowpack showed only limited ripening (e.g., snow density ≤ 0.30), it was possible to compile and compare 9 years of pre-melt snowpack chemistry.

Composite snow cores were taken with a Plexiglas cylinder (diameter = 14.5 cm) at 10 to 11 sites located at various elevations in the basin. The snow cores were transferred to clean polyethylene bags, weighed and thawed at room temperature for chemical analysis. Immediately thereafter, pH and specific conductivity were determined on all samples. Cations and nutrients were measured in accordance with methods outlined by the Department of the Environment (1979); anions were determined on a Dionex model 2010i ion chromatograph.

RESULTS AND DISCUSSION

The yearly water equivalent of the pre-melt snowpack ranged from 159 mm in 1983, to 377 mm in 1988 (Fig. 1). Snowmelt began in February from 1983 to 1985, and in March for the remaining 6 years of record.

Concentrations of major ions and nutrients in the pre-melt snowpack appeared to be regulated by the water content of the snow cover. Maximum levels of H^+, NH_4, SO_4, and NO_3 coincided with minimum values

of snowpack water equivalent (Fig. 2). Scavenging of acid precursors in the atmosphere is most effective during low precipitation events or at the onset of heavy snowfall; increasing precipitation may lead to a dilution of ion concentrations in the snowfall and consequently in the snowpack. The inverse relationship between precipitation quantity and ion concentration is analogous to that observed for some rain events at the TLW (Semkin and Jeffries, 1986a).

In all years, the composition of the snow cover was dominated by H^+, NO_3 and SO_4 which accounted for an average 70% of the total ionic content (Table 1). The importance of the SO_4 and NO_3 contribution to snowpack acidity was highlighted by the strong linear correlation between H^+ and these ions (Fig. 3). A common source, transport and/or deposition mechanism for NO_3 and SO_4 in the snowpack was also inferred by their significant linear relationship ($r = 0.83$).

Values of SO_4/NO_3 equivalent ratios less than 1.0 are common in the pre-melt snowpack. An average ratio of 0.88 ($S = 0.10$) was recorded for the 9 years of measurement at the TLW. Sirois and Vet (1988) similarly reported low winter (December-February) concentrations of wet and dry SO_4 relative to corresponding NO_3 levels in atmospheric deposition. They concluded that the seasonality of the deposition chemistry, i.e., maximum total NO_3 in the winter and fall and minimum total SO_4 loading in the winter, was related to variable emission patterns, transport winds, chemical conversion rates and dry deposition velocities during the year.

Temporal trends in snowpack ion concentration from 1980 to 1988 displayed considerable scatter for most species (Fig. 2). To decipher the chemical variability attributed to fluctuating levels of water equivalence, ion equivalent ratios were tabulated and evaluated. The trend of increasing H/SO_4 and decreasing SO_4/NO_3 equivalent ratios (Fig. 4) supported a hypothesis of increasing H^+ and NO_3 levels with respect to SO_4 in snowfall since 1980.

Volume-weighted concentrations of major ions and nutrients were calculated for precipitation at the CAPMoN (Canadian Air and Precipitation Monitoring Network) station located just beyond the southeastern boundary of the watershed. This site has been operational since 1980, and was dedicated to the measurement of both wet and dry atmospheric deposition (Sirois and Vet, 1988). For this study, the record of precipitation chemistry was selected to match the period of snowpack accumulation for the years 1982 to 1988. On an annual basis, there was considerable chemical variability in the pre-melt snowpack with respect to cumulative wet-only deposition (Fig. 5). In 5 of the 7 years, SO_4 levels in wet-only deposition exceeded snowpack concentrations; however, NO_3 and NH_4 showed the reverse trend with equal or higher concentrations in the snowpack. H^+ concentrations in the two media displayed no discernible pattern. By averaging data from all years, it was apparent that the annual mean concentration of major ions and nutrients in the snowpack was less than that measured in wet-only deposition (Table 2). The exceptions were Mg and K which were measured at or near detection levels thus obfuscating any

comparison between precipitation and snowpack. Of the main contributors to the ionic pool, H^+ and NO_3 displayed somewhat similar concentrations whereas SO_4 levels were much more reduced in the snow cover.

These results were unexpected in view of the potential contribution of dry deposition to the already high wet-only input. Earlier work at the TLW had shown that snowpack ion concentrations were greater than those of wet-only deposition. Semkin and Jeffries (1986b) reported snowpack/wet-only deposition ratios of 1.20, 1.12 and 1.07 for H^+, SO_4 and NO_3 respectively at a snow site directly adjacent to the precipitation chemistry station. Here physical and climatological differences were minimized. When considering the multi-station and multi-year data set, the discrepancy between snowpack and wet-only deposition could be attributed to a variety of factors. Inter-site variability can result from the type and abundance of forest cover, elevation, slope and aspect, wind effects, etc. Although Semkin and Jeffries (1988) had reported coefficients of variation of less than 10% for H^+, SO_4 and NO_3 at 11 sites in the pre-melt snowpack, the variability over the basin may have been high enough to offset comparison with the precipitation data at a single station. A second consideration was the possible loss of ions from the pre-melt, winter snowpack. While not previously observed at the TLW by the authors, ion movement out of the snow cover has been documented elsewhere (Jones and Bisson, 1984).

Water equivalence and precipitation quantity were combined with major ion and nutrient concentrations to produce mass loadings in the

snowpack and wet-only deposition. Annual loadings from 1980 to 1988 (Fig. 6) were quite variable but did reveal the predominant influence of water content in determining the ion content. Maximum water equivalent values in 1982 and 1988 coincided with peak snowpack loadings of the snowpack chemical constituents.

A comparison of snowpack loading and wet-only deposition produced results similar to that observed with ion concentrations, i.e., snowpack levels were generally lower for the major ions H^+, SO_4 and NO_3 (Table 3). As with concentrations, the poor agreement between the snowpack and precipitation loadings can, in part, be attributed to inter-site variability in the TLW basin. The particularly low mass loadings recorded in the 1985 snowpack relative to wet-only deposition resulted from rainfall late in the winter season. While the rain input was incorporated as wet-only deposition, rainfall would have passed directly through the permeable snow cover and not contributed to the snowpack loading. The mass input associated with late winter/early spring rain can be comparable to that of snowfall at the study site. Semkin and Jeffries (1986b) reported that 51%, 49% and 37% of the H^+, SO_4 and NO_3 respectively in spring meltwaters were derived from rainfall, an observation which emphasizes the importance of monitoring climatological conditions prior to sampling the pre-melt snowpack.

In terms of the acid precursors, the SO_4 and NO_3 loadings in the snow cover ranged from 3.6 to 8.5 meq/m^2 and 4.7 to 12.2 meq/m^2 respectively. Studies by Sirois and Vet (1988) at the watershed

suggested that the winter input via precipitation accounted for 14% and 27% of the total annual SO_4 and NO_3 deposition from the atmosphere. Adding an equal or even greater input via rainfall, especially for SO_4, supports the observation that spring run-off is a major event in the hydrogeochemical cycle at the TLW.

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Table 1. Average Composition of the Pre-Melt Snowpack in the TLW 1980-1988.

	Mean	Coefficient of Variation %
Snow depth (m)	0.96	19
Water Equivalent (mm)	272	27
Snow density	0.28	9
Conductivity (µS/cm)	15.8	17
H^+ (pH)	0.0321 (4.49)	34
Ca^{2+}	0.0068	46
Mg^{2+}	0.0023	74
Na^+	0.0036	58
K^+	0.0013	85
NH_4^+-N	0.0154	34
SO_4^{2-}	0.0223	22
NO_3^--N	0.0265	24
Cl^-	0.0051	71

Table 2. Comparison Between Ion Concentrations in the Pre-Melt Snowpack[1] and in Wet-Only Deposition[2] 1982-1988.

	Snowpack		Wet-Only Deposition		Snowpack/Wet-Only
	$\bar{x}$	S	$\bar{x}$	S	
H_2O	283.9	77.8	290.6	52.2	0.98
H^+	0.0345	0.0113	0.0359	0.0042	0.96
Ca^{2+}	0.0063	0.0029	0.0065	0.0018	0.97
Mg^{2+}	0.0022	0.0018	0.0018	0.0006	1.22
Na^+	0.0034	0.0021	0.0055	0.0050	0.62
K^+	0.0010	0.0007	0.0009	0.0005	1.11
NH_4^+	0.0160	0.0059	0.0173	0.0057	0.92
NO_3^-	0.0276	0.0066	0.0306	0.0057	0.90
SO_4^{2-}	0.0223	0.0055	0.0301	0.0078	0.74
Cl^-	0.0037	0.0022	0.0056	0.0034	0.66
SO_4/NO_3	0.85	0.08	1.00	0.24	

[1]Each year of snowpack data represents the mean of 11 sites in the TLW.
[2]Concentrations were volume-weighted over the period of snowpack accumulation (i.e., pre-melt) for each year.

Table 3. Annual Comparison of H^+, SO_4 and NO_3 Loadings (meq/m^2) in the Pre-Melt Snowpack and Wet-Only Deposition.

Year	H^+ Snowpack	H^+ Wet-Only	Snowpack/ Wet-Only	SO_4 Snowpack	SO_4 Wet-Only	Snowpack/ Wet-Only	NO_3 Snowpack	NO_3 Wet-Only	Snowpack/ Wet-Only
1982	9.50	12.21	0.78	8.38	9.04	0.93	11.77	10.42	1.13
1983	8.82	8.66	1.02	5.10	9.35	0.55	5.35	6.85	0.78
1984	10.43	9.20	1.13	5.56	7.87	0.71	6.79	7.78	0.87
1985	4.97	10.53	0.47	3.61	9.37	0.39	4.68	9.57	0.49
1986	9.02	11.86	0.76	6.06	8.08	0.75	6.18	6.07	1.02
1987	9.28	8.36	1.11	5.58	5.56	1.00	7.19	8.00	0.90
1988	12.37	11.26	1.10	8.45	10.10	0.84	12.18	13.00	0.94

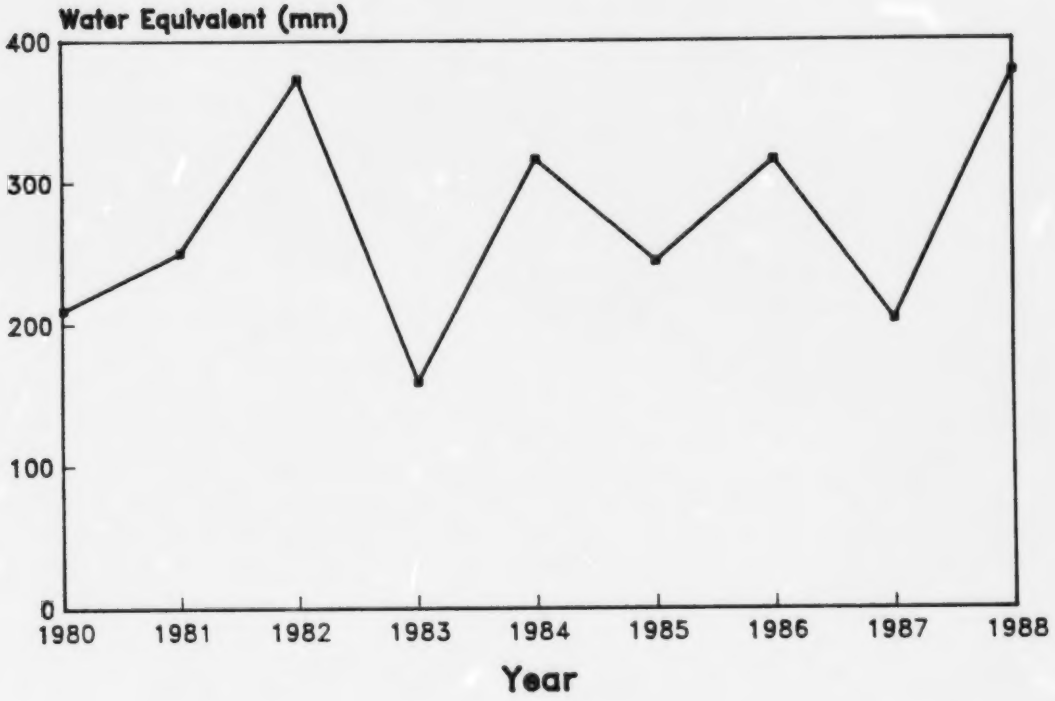


Fig. 1. Snowpack Water Equivalent 1980-1988

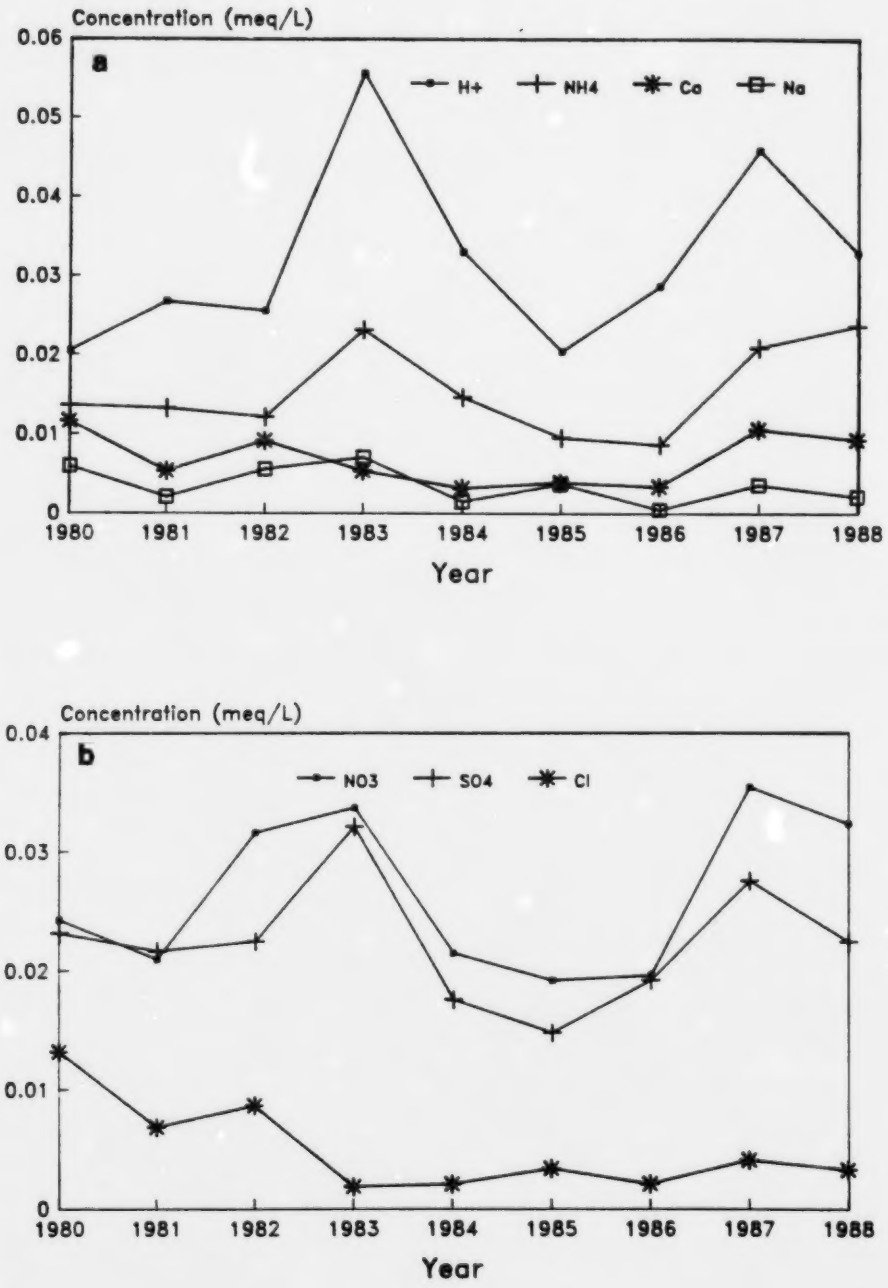


Fig. 2. Annual Variation in Major Ion Concentrations in the Snowpack: (a) Cations, (b) Anions.

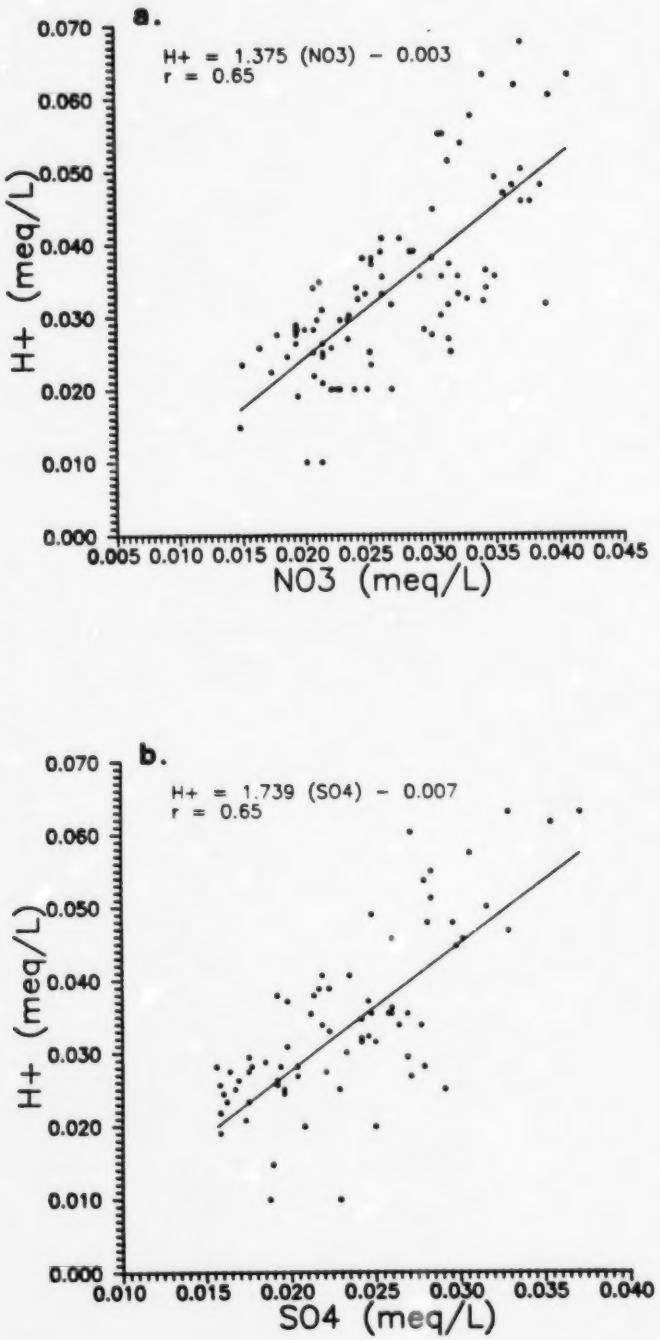


Fig. 3. Relationship Between Snowpack H^+ Concentration and (a) NO_3, (b) SO_4.

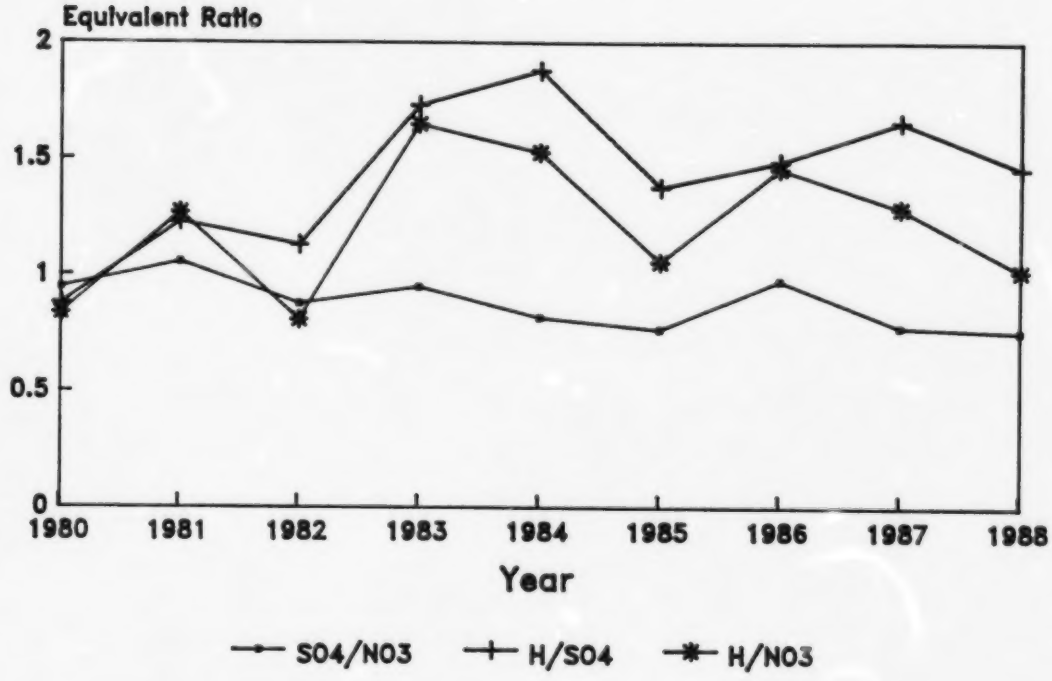


Fig. 4. Ion Equivalent Ratios in the Pre-Melt Snowpack, 1980-1988.

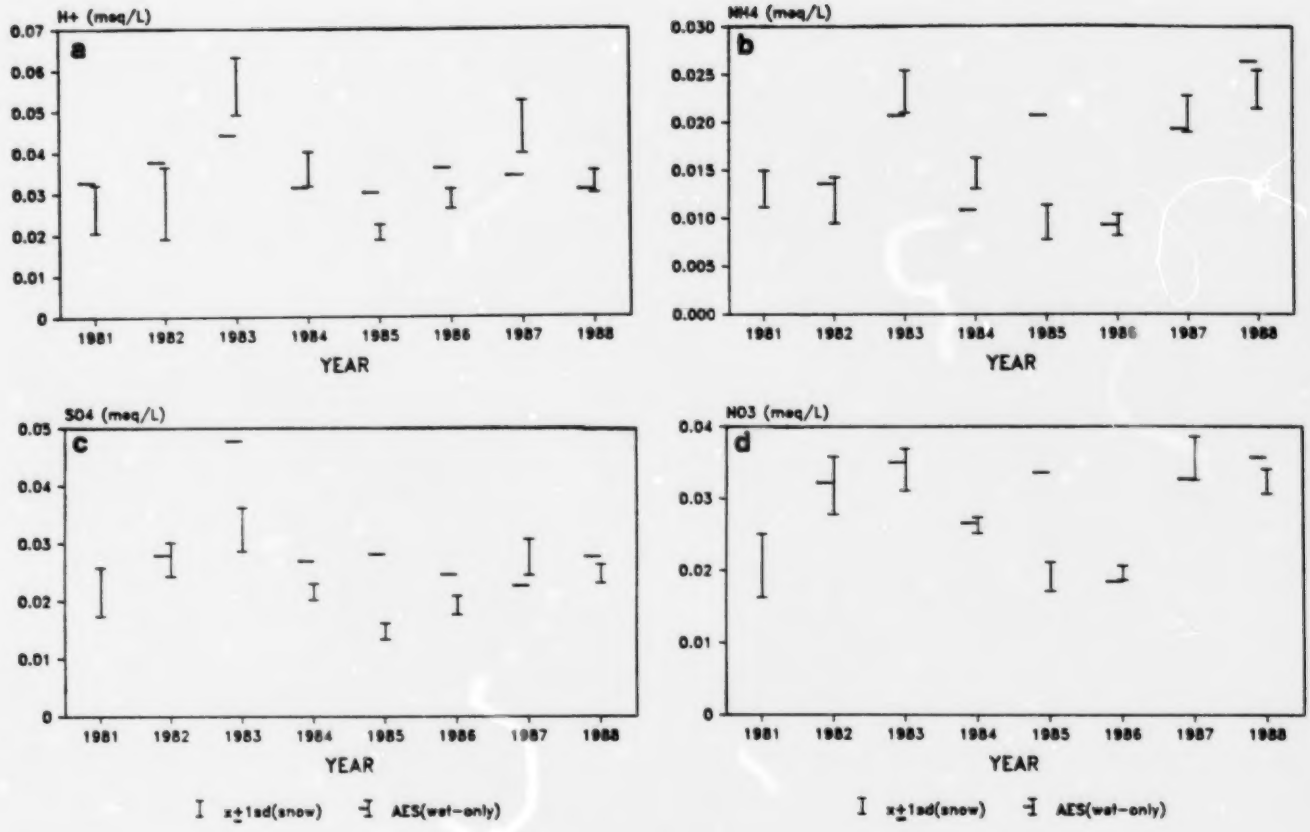
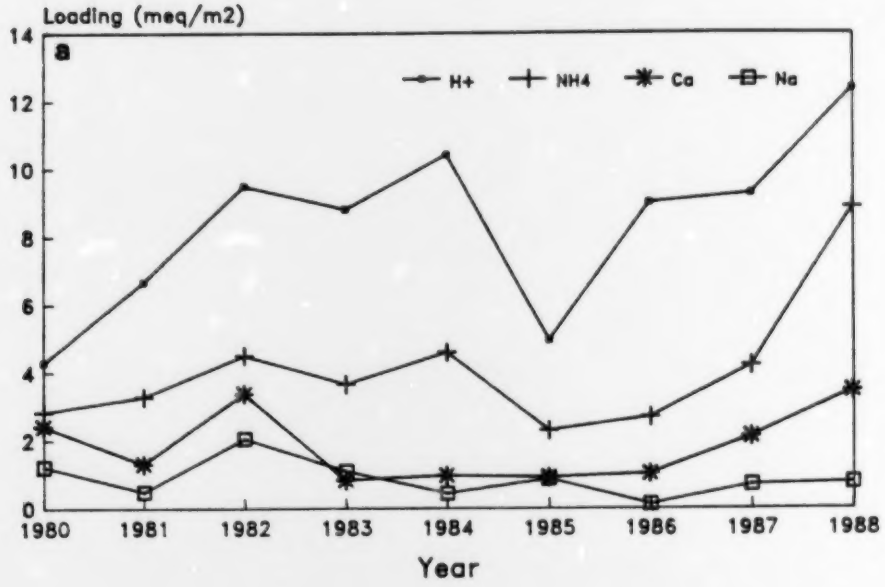


Fig. 5. Annual Comparison of Major Ion Concentrations in Pre-Melt Snowpack and Wet-Only Atmospheric Deposition: (a) H^+, (b) NH_4, (c) SO_4, (d) NO_3.



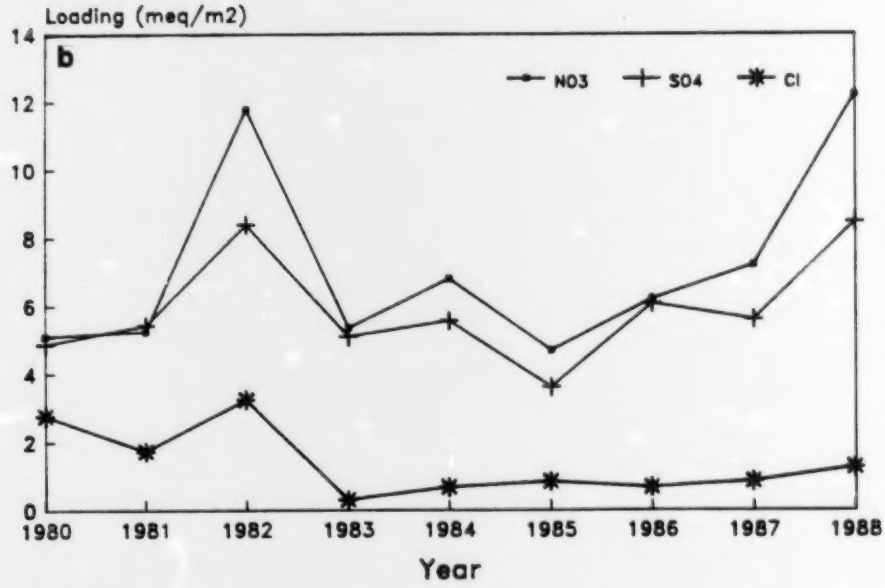


Fig. 6. Major Ion Loadings in the Snowpack, 1980-1988: (a) Cations, (b) Anions.